

MODES OF OCCURRENCE OF TRACE ELEMENTS IN COAL: RESULTS FROM AN INTERNATIONAL COLLABORATIVE PROGRAMME

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Keywords: Coal, Trace Elements, Modes of Occurrence

INTRODUCTION

A collaborative research project on the modes of occurrence of trace elements in coal was set up within the IEA implementing agreement on Coal Combustion Sciences. Les Dale of CSIRO, Australia, coordinated the project. Participants in the project were requested to determine the modes of occurrence of trace elements of environmental significance using their chosen methodology. The aim was to determine not only the modes of occurrence but also to obtain data that could be compared and contrasted. The final reports were then sent to IEA Coal Research to form the basis of a critical review of the project (Davidson, 2000). They have been published on the CD-ROM that accompanies the overall final report.

The collaborative programme was set up because the participants believe that understanding the modes of occurrence in coal is essential for developing reliable models to predict the behaviour of elements during in-ground leaching, weathering, coal cleaning, or combustion. Modelling the behaviour of the trace elements is necessary to provide an accurate evaluation of the environmental and human health impacts, technological impacts, and economic by-product potential of coal use (Willett and others, 2000). Knowledge of the mineralogical residences or modes of occurrence of trace elements in coal is very important in the understanding of mechanisms by which trace elements are enriched in fly ash and are found in flue gas (Dale and Chapman, 1999). This is because the behaviour of the trace elements in coal-fired power stations is partly dependent on the mode of occurrence of the elements in the original coal (Wigley and others, 2000).

THE PARTICIPATING LABORATORIES

Laboratories in Australia, Canada, Spain, the United Kingdom, and the USA participated in the collaborative study:

| | |
|-----------|---|
| Australia | CSIRO, Division of Energy Technology, Lucas Heights, NSW (Dale and Chapman, 1999) |
| Canada | Geological Survey of Canada, Energy and Environment Division, Calgary, Alberta (Goodarzi and others, 1999). |
| Spain | Institute of Earth Sciences "Jaume Almera", CSIC, Barcelona (Querol and others, 1999) |
| UK | University of Sheffield, Centre for Analytical Sciences, Sheffield (Spears and others, 1998) |
| UK | Imperial College of Science, Technology and Medicine, Department of Materials, London (Wigley and others, 2000) |
| USA | Energy & Environmental Research Center, University of North Dakota, Grand Forks, ND (Galbreath and others, 1999) |
| USA | University of Kentucky, Department of Chemical and Materials Engineering, Lexington, KY (Huggins, 1999) |
| USA | US Geological Survey, Reston, VA (Willett and others, 2000) |

THE COALS SELECTED

In the initial stages of the project, three different coal samples were distributed. A fourth coal, from a mine in Nova Scotia, Eastern Canada was distributed to participants about a year after the first three coals were distributed. Not all the collaborating laboratories were able to study all four samples, but most were able to study the Australian, British, and US samples. The coals selected were:

- Wyee coal - a high volatile bituminous Australian coal,
- Gascoigne Wood - a UK bituminous coal from a 2 tonne batch from power station feed,
- Illinois No. 6 - a high volatile US bituminous coal, and an
- Eastern Canadian coal - also high volatile bituminous.

Table 1 lists some analytical data provided by Goodarzi and others (1999).

Table 1 Proximate and ultimate analyses of the four coals (Goodarzi and others, 1999)

| | Wyee, Australia | Eastern Canadian | Gascoigne Wood, UK | Illinois No. 6, US |
|----------------------------|--------------------|---------------------|-----------------------|-----------------------|
| Proximate analysis, wt% ar | | | | |
| Moisture | 2.6 | 1.33 | 3.2 | 3.3 |
| Ash | 23.0 | 9.86 | 15.2 | 10.1 |
| Volatile matter | 27.1 | 31.96 | 29.6 | 36.1 |
| Total sulphur | 0.37 | 3 | 1.16 | 3.4 |
| Ultimate analysis, wt% daf | | | | |
| Carbon | 63.62 | 75.31 | 69.2 | 69.84 |
| Nitrogen | 1.31 | 1.38 | 1.58 | 1.36 |
| Sulphur | 0.38 | 3.00 | 1.20 | 3.52 |
| Hydrogen | 3.46 | 4.53 | 4.03 | 4.27 |
| Oxygen | 7.62 | 6.12 | 8.25 | 10.57 |
| Sulphur forms, wt% | | | | |
| Sulphate S | 0.01 | 0.30 | 0.08 | 0.08 |
| Pyritic S | 0.05 | 1.70 | 0.32 | 1.30 |
| Organic S | 0.31 | 1.00 | 0.76 | 2.02 |

MINERALOGY

Goodarzi and others (1999) provide a comprehensive account of the mineralogies of the coals used in these studies. Most of the collaborating laboratories analysed the mineral composition of the coals although different methods were used. The analyses of the bulk ash contents are in reasonably close agreement for all the laboratories that provided data. However, some differences emerge in the detailed data. Huggins (1999) reports values for the float/tailings fractions and their ash content for separations performed using a Denver flotation cell. Galbreath and others (1999) separated the coals using a 1.6 specific gravity solution for the Wyee coal and a 1.45 specific gravity solution for the other three. The data are compared in Table 2 that lists the percentage ash remaining in each fraction.

Table 2 Percentage ash separation analyses (Galbreath and others, 1999; Huggins, 1999)

| | Wyee, Australia | Eastern Canadian | Gascoigne Wood, UK | Illinois No. 6, US |
|----------------------|--------------------|---------------------|-----------------------|-----------------------|
| Density sink | 73 | 76 | 73 | 54 |
| Denver cell tailings | 40 | 49 | 69 | 21 |
| Density float | 27 | 24 | 27 | 46 |
| Denver cell float | 60 | 51 | 31 | 79 |

The differences, except for the Gascoigne Wood coal, are considerable but most likely reflect physical differences in the separation methods. The differences in the separations by different mechanical separations could possibly lead to different assignments of the trace element modes of occurrence. It would be expected that a greater proportion of trace elements will be found in the maceral-rich fraction from Denver cell flotation except, possibly, for the Gascoigne Wood coal. Although, when at least 24% of the ash is encountered within the maceral-rich float fractions, this is scarcely evidence for 'maceral-association' rather than 'mineral-association' with minerals dispersed within the bulk of the organic matter. Galbreath and others (1999) observed that most of the minerals in their float fractions were present as tiny ($< 5 \mu\text{m}$ in the longest dimension) inclusions within coal particles. Most of the trace elements are enriched to some extent in the tailings fractions (Goodarzi and others, 1999) but, even when depleted in the float compared with the coal, a greater proportion of the trace elements often remains there.

THE TRACE ELEMENTS COMPARED

Not every trace element was analysed by every laboratory so that comparisons among them have to be made using a restricted set. The eleven elements identified in the US Clean Air Act Amendments (CAAA) of 1990 as potentially 'hazardous air pollutants' with the addition of copper and zinc formed the basis of the overview report:

Beryllium, chromium, manganese, cobalt, nickel, copper, zinc, arsenic, selenium, cadmium, antimony, mercury, and lead.

A range of analytical techniques was employed in the qualitative and quantitative analysis of the elements in the coals and their fractions. Generally, the data for the concentrations of these trace elements in the whole coal were in reasonably good agreement

SAMPLE FRACTIONATION

In order to determine the modes of occurrence of the trace elements in the samples, the coals were fractionated using variants of two techniques - **physical separation** and **sequential leaching**. As noted above, Galbreath and others (1999) used a float/sink density separation method with specific gravity solutions composed of mixtures of reagent-grade tetrachloroethylene and petroleum ether. After mixing and centrifugation, the float and sink samples were separated, dried in a nitrogen-purged oven and weighed. Float fractions were composed predominantly of organic (maceral-rich) with small proportions of minerals. Most minerals in the float fractions were present as tiny ($< 5 \mu\text{m}$ in the longest dimension) inclusions within the coal particles. However, as shown in Table 2, the minerals in the float fractions still accounted for about a quarter of the total in three coals (Wyee, Eastern Canadian, and Gascoigne Wood) and nearly half in the Illinois No. 6 coal. The sink fractions were composed predominantly of larger discrete mineral grains.

Querol and others (1999) also used density fractionation. They obtained seven density fractions between < 1.3 and $> 2.8 \text{ g/cm}^3$ by using heavy liquid mixtures of bromoform, tetrachloroethylene, and xylene. It was noted that the density fractionation technique was developed for the study of high mineral matter coals. The relatively low mineral matter content of the coals in the collaborative study made complete isolation of the minerals difficult. Further, as noted above, it was also found that the mineral matter was finely dispersed in the organic matter that consequently made good density separation. It was for such reasons that chemical treatments were also used to isolate or extract mineral phases from the density fraction, specifically to extract gypsum from the $2.0\text{--}2.4 \text{ g/cm}^3$ fraction of the Gascoigne Wood coal and to enrich pyrite by acidic attack on calcite in the $> 2.8 \text{ g/cm}^3$ fraction of the Illinois No. 6 coal (Querol and others, 2000). Using this separation technique, Querol and others (1999) were able to assign the trace elements into the following affinity categories:

- organic matter (OM), density fraction < 1.3 ;
- aluminosilicates, mainly clays (ALS);
- sulphates (GYP);
- sulphides, selenides, and arsenides (PY), density fraction > 2.8 ;
- iron carbonate (CARB);
- heavy minerals (HM); and
- phosphates (PHOS).

Table 2 in Querol and others' (1999) report shows more details of the density fractions used for each coal. Querol and others (2000) later modified their density fractionation data by using a mathematical deconvolution of the chemical analyses of the whole coals and their density fractions. The mathematical deconvolution calculates the amount of organically associated elements in each density fraction. It is based on a method developed by Klika and Kolomaznik (2000) and uses the following data from the float/sink experiments:

1. mass of the coal fractions,
2. sum of crystalline phases and ash content,
3. concentrations of the trace elements in each of the coal fractions,
4. concentrations of sulphide and carbonate in each fraction.

This enables the calculation of the percentage trace element affinity to the organic part of the coal. The concentrations of the elements in the sulphide and carbonate fractions of the coal are used in a semiquantitative determination of the elemental affinities in the inorganic parts of the coal.

Huggins (1999) used a hybrid physical separation method in which the coal samples were first separated into float and tailings fractions using a Denver column flotation cell. A small fraction of the tailings product was then further subdivided by a float/sink density separation technique using bromoform with a specific gravity of 2.875. As a result of these separations, the as-received coal (RAW) was split into four fractions:

- the tailings (TAILS) from the Denver cell flotation,
- an "organic fraction" (ORG) representing the float fraction from the Denver cell,
- a "heavy minerals" fraction (HYM) representing the fraction of the Denver cell tailings that sank in bromoform, and
- a "clay" fraction (CLAY) representing the fraction of the Denver cell tailings that floated in bromoform.

The bromoform separations were not very successful. As a result, with the exception 1-2% of HYM from the Illinois No. 6 coal, the TAILS and CLAY fractions were essentially the same. The float and tailings fractions from the Denver cell were also analysed by Goodarzi and others (1999).

The other laboratories involved in the study used different sequential leaching separations. These are based on the standard method of determining the forms of sulphur in coal. Dale and Chapman (1999) used the following sequence:

1. 4.3 M hydrochloric acid (HCl) at 80°C for two hours. This dissolves oxides, carbonates, and monosulphides. The residue was then treated with
2. 0.5 M nitric acid (HNO₃) at 80°C for two hours. This dissolves sulphides (pyrite). The residue was then treated with
3. 10 ml 40% hydrofluoric acid (HF) and 1 ml concentrated HCl at 60-70°C for 1 hour. 5 ml HCl and 5 ml water were then added and the mixture heated at 60-70°C for a further 1 hour. This dissolves the silicates.

The various solutions were analysed for specific trace element concentrations and the "organic" residue was also analysed. The selectivity of the pyrite leaching (stage 2) for the Illinois No. 6 coal was investigated by X-ray diffraction. It was verified that 0.5 M HNO₃ removed 100% of the pyrite.

Although not used in the study of the IEA collaborative programme coals, Dale and others (1999) later introduced an initial stage in which coal samples were treated with 1M ammonium acetate (CH₃COONH₄) at 80°C for two hours. This is similar to the first stage of the USGS sequence used by Willett and others (2000):

1. 1N ammonium acetate (CH₃COONH₄). This removes loosely bound ions that may be organically associated or ions absorbed on clays and dissolves some calcite. The residue was then treated with
2. 3N HCl. This removes carbonates, such as calcite, and monosulphides. The residue was then treated with
3. concentrated (48%) HF. This removes silicates, including quartz and clay minerals. The residue was then treated with
4. 2N HNO₃. This primarily removes disulphides such as pyrite.

It was recognised that some silicates, such as zircon, may be resistant to the HF leaching in stage 3. The residue left includes these, other insoluble minerals, and elements "shielded" from the solvents, together with the organic portions of the coal. It should be noted that the ash yield of the residual leached coal was commonly less than 0.3 wt%, suggesting little in the way of shielded and insoluble phases in most coals.

Spears and others (1998) used the sequence:

1. shake with deionised water for up to 12 hours. This removes elements present in pore fluids and soluble minerals. The residue is shaken with
2. dilute HCl for up to 12 hours. This removes carbonates (mainly calcite), exchangeable cations and monosulphides. The residue is shaken with
3. dilute HNO₃ (5%) for up to 12 hours. This removes carbonates (mainly dolomite and ankerite) and some pyrite. The residue is shaken with
4. concentrated, cold HNO₃ and allowed to stand for up to 12 hours. This removes the remaining pyrite. The solid remaining is digested with
5. concentrated HNO₃ with microwave heating. This digests the organic matter. Any remaining solid is digested with
6. concentrated HCl and HF with microwave heating. This digests the silicates.

Unlike the other sequential leaching procedures, this method completely digests the coal sample leaving no "organic" residue. Some inherent problems in the technique were recognised by Spears and others (1998). For example, some of the pyrite is released in stage 3 but not quantitatively, the rest is removed in stage 4. The silicates and the organic matter will also have been partially attacked in the early stages. There is also the problem that mineral groups, such as carbonates and sulphides, do not behave uniformly.

Obviously, the data from the different groups are not strictly comparable since they were obtained from different of separation techniques ranging from simple fractionation into float and sink fractions to more complex fractionation either by density fractionation or selective leaching. Nevertheless, comparisons needed to be made, even at the risk of misinterpreting some of the data. The comparisons are published in the final overview report (Davidson, 2000) and some of them will be discussed in the presentation.

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